The Chemistry of Aldehydes & Ketones
February 12, 2020

- Synthesis of aldehydes: review of previous methods and introduction to DIBAL.
- Synthesis of ketones: review of previous methods and intro to the reaction of nitriles with RMgX or RLi.
- Acetals & ketals, including their sulfur analogs.
- The addition of amines to aldehydes and ketones.

110b Teaching Fellows: Felipe Becerril, Christina Beck, Isabelle Cheng, Junha Gu, Nathalie Hong, Shy Lavasani, Allison Liu, Casey Morrison, Jerusalem Nerayo, Eric Tang, Baili Zhong, Martín Acosta Parra.

Chemistry Seminar! Prof. Doug Grotjahn, San Diego State University, "When Two are Better than One: Bifunctional Catalysts that Move Protons for Organic Chemistry and Energy." Tuesday, February 11, 11:00 am, Seaver North Auditorium.

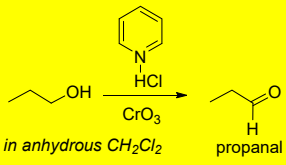
O'Leary office hours: T/Th 9:30-10:00 am, SN 208.

O'Leary's evening review session: Wednesdays 7:00 PM, SN Aud. **Course website**: http://pages.pomona.edu/~djo04747/110/

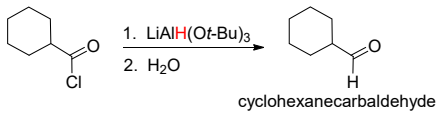
Suggested Problems for Exam 2. 10e: 16.20, 24, 30, 33, 35, 41, 44, 45, 47. 11e: 16.23, 27, 33, 36, 38, 44, 47, 48, 50. 10e/11e: 17.20, 17.28, 17.31, 17.33, 17.35, 17.38, 17.41, 17.42, 17.47.

Synthesis of Aldehydes: An Overview

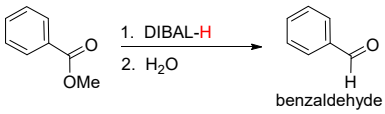
Recall the PCC oxidation of 1° alcohols:



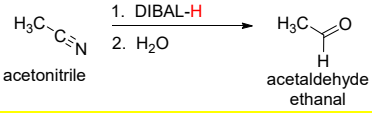
Lithium tri-tert-butoxyaluminum hydride reduction:



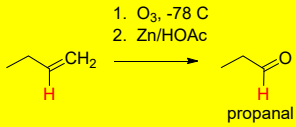
Diisobutylaluminum hydride (DIBAL-H) reduction of esters:

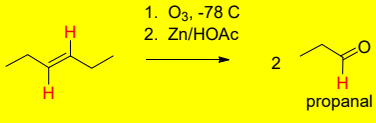


Diisobutylaluminum hydride (DIBAL-H) reduction of nitriles:



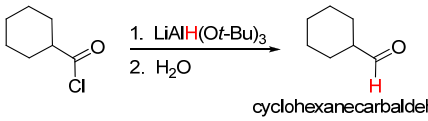
Ozonolysis of alkenes:



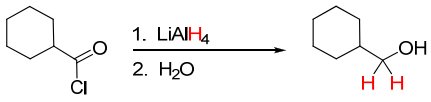


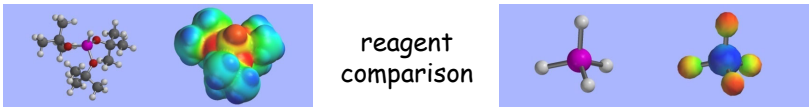
Reduction of Acid Chlorides with $LiAlH(Ot\text{-}Bu)_3$

Lithium tri-tert-butoxyaluminum hydride reduction:

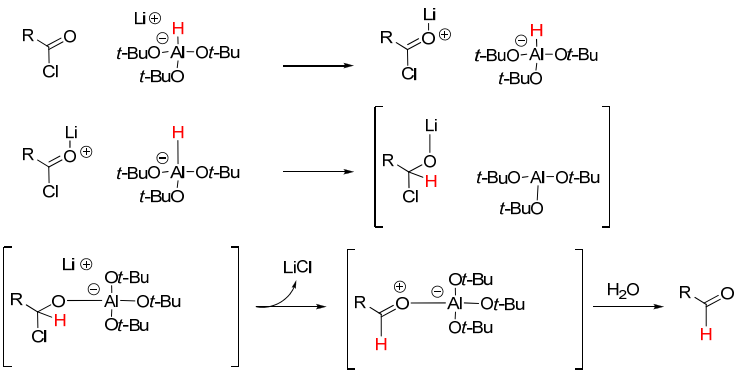


Note: *Lithium aluminum hydride gives the alcohol:*



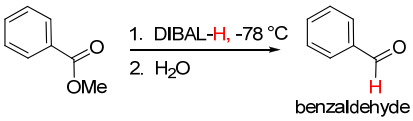


Mechanism:

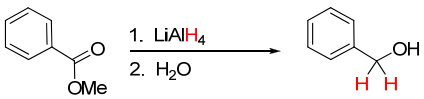


Reduction of Esters with DIBAL-H

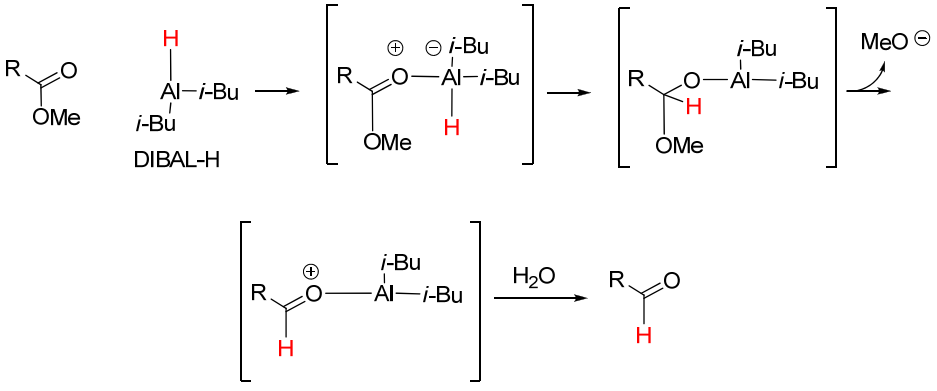
Diisobutylaluminum hydride (DIBAL-H) reduction of esters:



Note: *Lithium aluminum hydride gives the alcohol:*

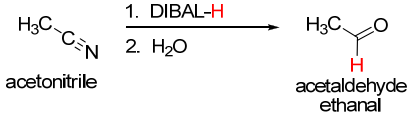


Mechanism:

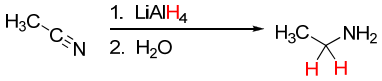


Reduction of Nitriles with DIBAL-H

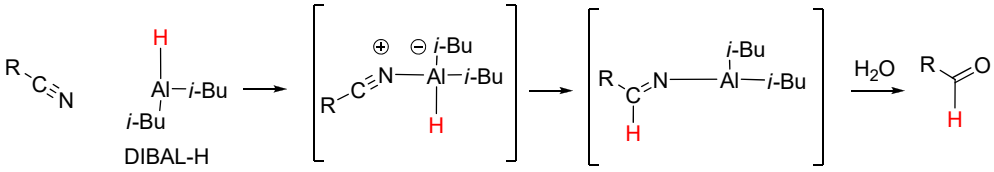
Diisobutylaluminum hydride (DIBAL-H) reduction of nitriles:



Note: *Lithium aluminum hydride gives the amine:*

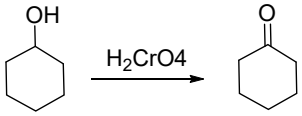


Mechanism:

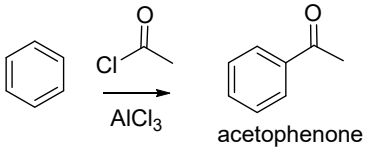


Synthesis of Ketones: An Overview

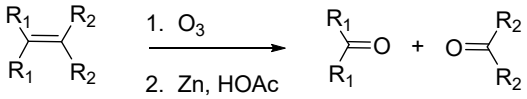
Recall the Jones oxidation of 2° alcohols:



Recall the Friedel-Crafts Reaction:



Ozonolysis of alkenes:



Reaction of nitriles with Grignards or Alkyl Lithium reagents:

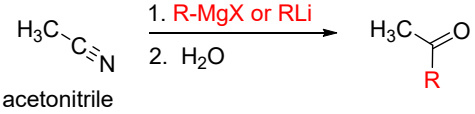
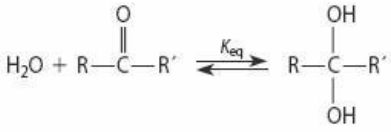
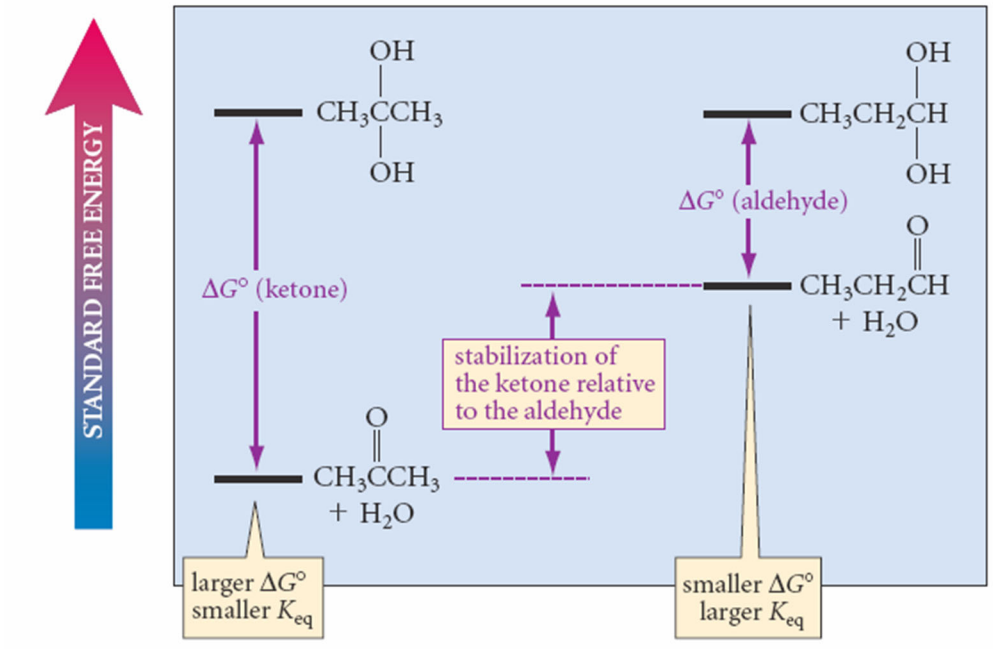
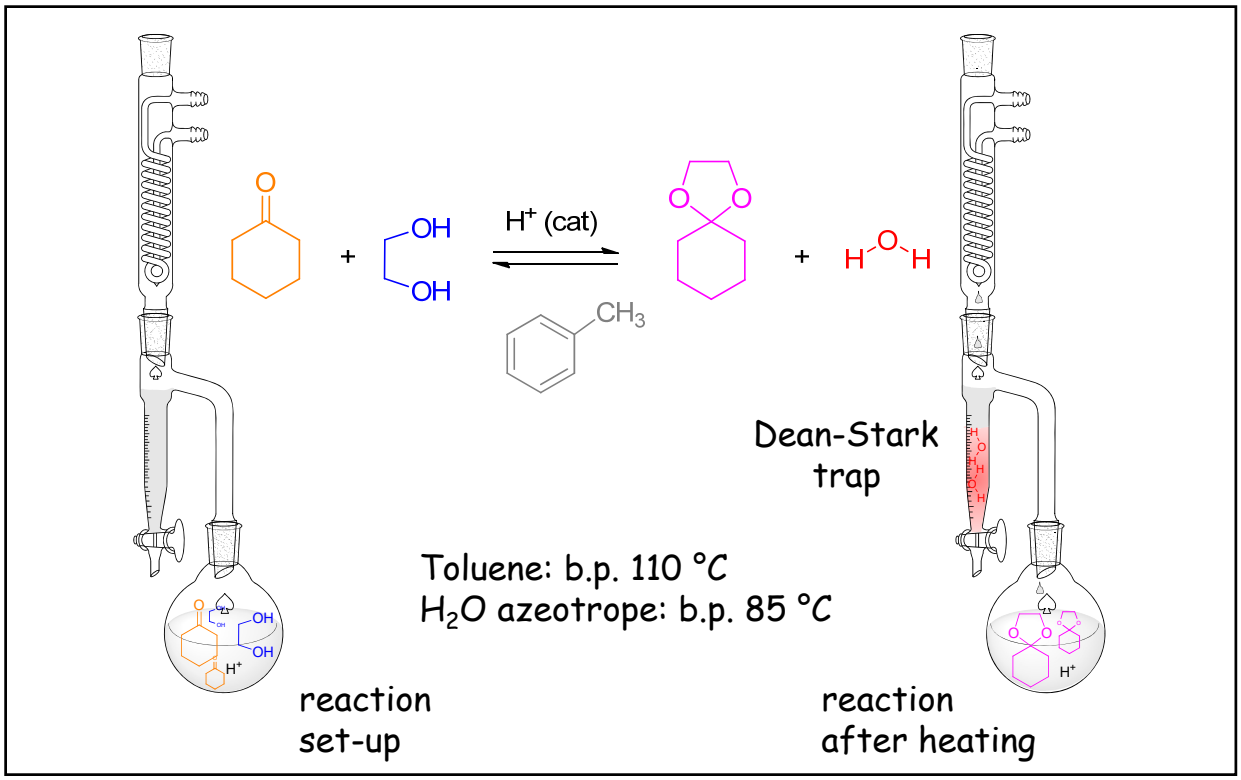


TABLE 19.2 Equilibrium Constants for Hydration of Aldehydes and Ketones

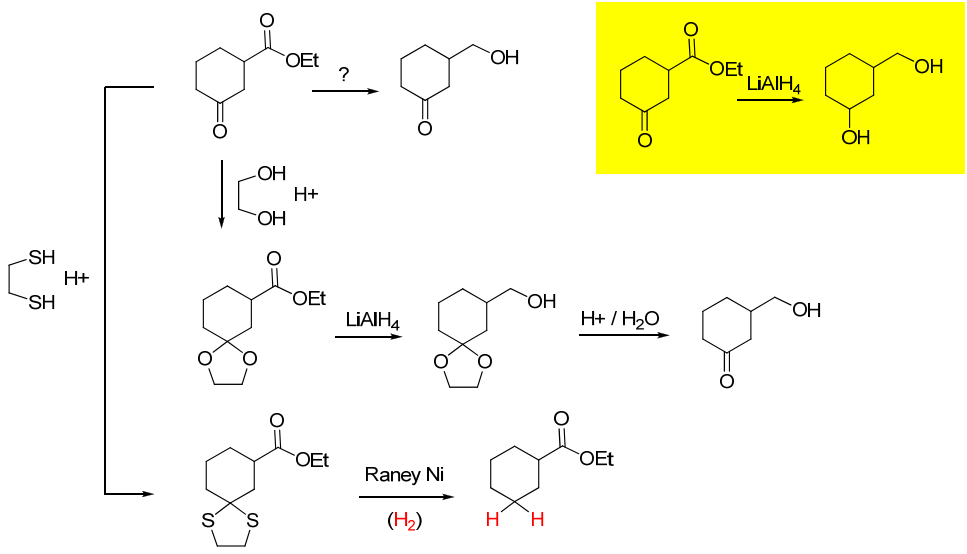


Aldehydes	K_{eq}	Ketones	K_{eq}
$H_2C{=}O$	2.2×10^{3}	$(CH_3)_2C{=}O$	1.4×10^{-3}
$CH_3CH{=}O$	1.0		
$(CH_3)_2CHCH{=}O$	0.5–1.0	$Ph{-}C(=O){-}CH_3$	6.6×10^{-6}
$PhCH{=}O$	8.3×10^{-3}	$Ph_2C{=}O$	1.2×10^{-7}
$ClCH_2CH{=}O$	37	$(ClCH_2)_2C{=}O$	10
$Cl_3CCH{=}O$	2.8×10^{4}	$(CF_3)_2C{=}O$	too large to measure

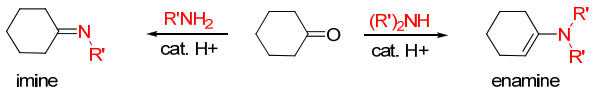


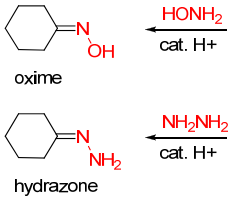


Acetals and Ketals: Synthetic Applications

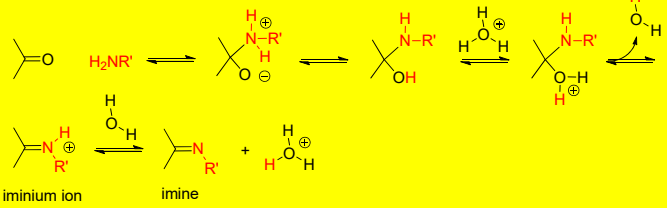


Addition of Primary and Secondary Amines to Aldehydes & Ketones: Imines & Enamines

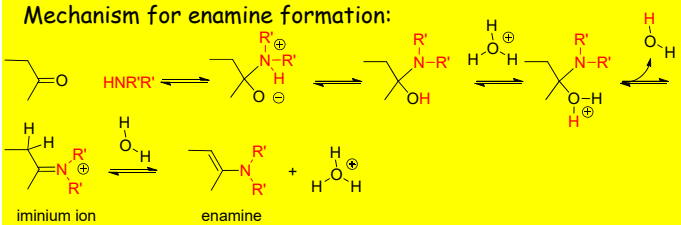




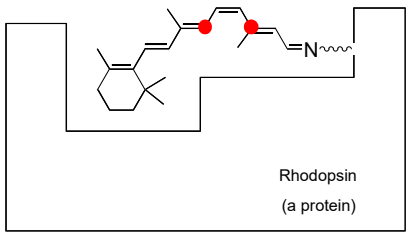
Mechanism for imine formation:

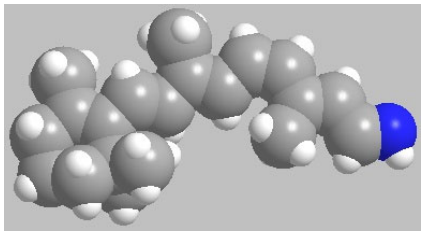


Mechanism for enamine formation:

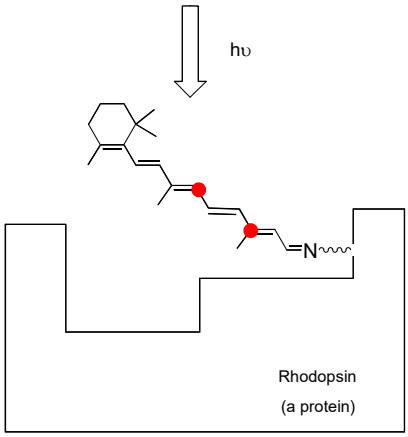


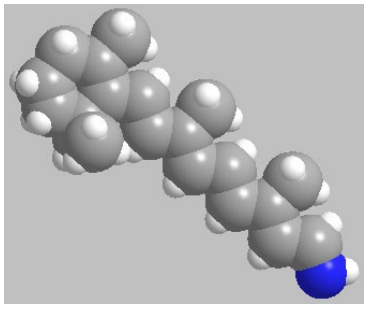
Organic Chemistry of Vision





Cis-retinal





Trans-retinal